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A view on the future of mixed oxide catalysts The case of heteropolyacids (polyoxometalates) and perovskites

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Abstract

Recent progress of mixed oxide catalysts has been surveyed briefly, and future opportunities of catalytic technology are discussed, taking for example solid heteropolyacid and perovskite catalysts, where some promising signs for the future are noted. It was stressed that much more efforts should be directed to develop useful catalysts in practical applications, in order to accelerate the progress of catalytic science and technology.

Keywords: Heteropolyacids; Polyoxometalates; Perovskites; Catalyst design; Mixed oxides

1. Introduction

The development of high-performance catalysts is still very important for chemical technologies that supply useful substances to the society and assist keeping the environment healthy. However, it recently appears that the progress of catalytic science and technology is slower and epoch-making innovations in catalytic technology are fewer, particularly in heterogeneous catalysts, although the number of papers maintains a high rate of increase. The slow progress and few innovations may be connected with each other. In my view, a catalyst can be called a catalyst only when it catalyzes useful reactions in practical application. This is the same as that a technology is called a technology when it works well in the real world. Hence, the reason why the progress of catalytic science and technology is recently slow is probably because sufficient efforts are not devoted to develop novel catalysts for practical applications. We may lack more than before the collaboration between fundamental and applied researches, and probably our selections of target reactions have not been good enough.

In the above respect, the value of R&D on practical catalysts (these are important as described above) may be expressed, for example, by

$$\text{value} = \frac{I}{1+D} \tag{1}$$

where I is the impact on catalytic technology, such as novelty, expected profit, greenness, etc., and D is the distance (length of period) to the realization in the real world. This equation is conceptual, just indicating that the value, V, increases with the impact, I, and decreases with the distance, D. A similar equation may be proposed for fundamental research for practical catalysts, as well.

In this short article, the progress of mixed oxide catalysts is surveyed focusing on heteropolyacid and perovskite catalysts. It is also attempted to pick up several achievements that may lead to future innovative catalytic technologies and important problems to be solved by basic research for the progress of the technologies.

My personal belief is that the breakthroughs in the design of heterogeneous catalysts (undoubtedly for practical applications) can be brought about by the design at the atomic/molecular level. Although this is not an easy task, our efforts have been devoted to construct the basis for

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this design by choosing crystalline heteropolyacid and perovskite mixed oxides, as described in our recent accounts [1–3]. Our basic concept is that mixed oxides having well characterized structure, at least in the solid bulk, are suitable for the catalyst design at the atomic/molecular level.

2. Solid heteropolyacid (polyoxometalates) catalysts

2.1. General remarks on solid heteroplyacid (HPA) catalysts

Fundamentals that make possible the design of solid HPA catalysts at the atomic/molecular level have been fairly well established. First, several groups including our group showed that the molecular nature of heteropolyanion is maintained in the solid state, if necessary caution is paid, and that their acid and redox properties can be controlled in a regular way by changing the atomic composition. Second, we found that the presence of hierarchical structures (primary, secondary and tertiary structures) and three different modes of catalysis (surface-type, pseudoliquid (bulk-type I), and bulk-type II) [1,4,5]. We demonstrated that these are the indispensable basic concepts for the understanding and design of solid HPA catalysts. For example, due to the pseudoliquid behavior that we first reported in 1979 and summarized in 1987 [5], not only very high catalytic activities are obtained, but also reaction mechanisms are elucidated at the molecular level. Recently the locations and dynamic behavior of acidic protons have been spectroscopically clarified [6,7]. In addition, precise control of pore size was made possible for Cs and K salts through the understanding of their nanostructures [1,4].

There are already more than seven large-scale industrial processes using HPA catalysts, mostly in Japan. A recent topic in industry is that remarkable improvement was reported for the process of ethyl acetate production catalyzed by HPA (Showa Denko), although the plant already started several years ago.

2.2. Acid catalysis of HPA

2.2.1. Recent progress

It has been demonstrated that the catalytic activities for surface-type reactions are correlated proportionally to the surface acidity and those for the reactions in pseudoliquid to the bulk acidity [1,4]. In the former case, we found that Cs2.5 ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) is much more active than the traditional solid acids for many liquid-phase organic reactions of surface-type and that precise control of nanopores of acidic Cs salts brings about remarkable shape selectivity that differentiate the molecular size of reactants [1,4].

The followings are two recent interesting findings for practical application of solid HPA in liquid phase. Efficient solid catalysts are very desirable in the wide range of applications in the syntheses of fine chemicals. Here, the *E*-factors (by-product/main product ratios proposed by Sheldon) are very large (10–100), due to the multi-step syntheses and to mass and energy consumption during separation and purification. An example shown in Fig. 1 [8] demonstrates that usage of solvents is tremendous.

2.2.1.1. Firm immobilization of Cs2.5 on silica [9]. Cs2.5 is almost insoluble in water, but after agitation during reaction the surface layer of Cs2.5 dissolves slightly and also partly comes off as nanoparticles into solution. In addition, the particles of Cs2.5 are so small that their separation by filtration is difficult. Recently, Okuhara et al. found that Cs2.5 nanoparticles bound to the amino group of a coupling reagent, 3-aminopropyltetraethoxysilane (APTS), that is chemically bonded to the surface of silica (APTS:silica = 14:86) (Fig. 2), showed only a loss of less than 0.02% and were easily separable, maintaining more than 90% of the catalytic activity of Cs2.5.

2.2.1.2. Water-tolerant catalysis of Cs2.5 [10]. According to the adsorption of water, the hydrophobicity was presumed to be in the order of HZSM-5 (Si/Al = 628) > HZSM-5 (Si/Al = 40) = Cs2.5 > silica–alumina. Owing to the moderate hydrophobicity, Cs2.5 shows a high catalytic activity for organic reactions in water like hydration of alkenes and hydrolysis of oligosugars (Table 1).

2.2.2. Important problems and a topic

(a) Crystalline bulk HPA catalysts (without supports or additives) are very talented catalysts for various organic reactions. But as they show rather ‘‘strong and unique character’’, fine-tuning of acidity and choice of adequate reaction systems (reactions themselves and reaction conditions) are crucial.

(b) The structure and acidic properties of supported HPA are very important for practical applications, but they have little been clarified. The control of the HPA–

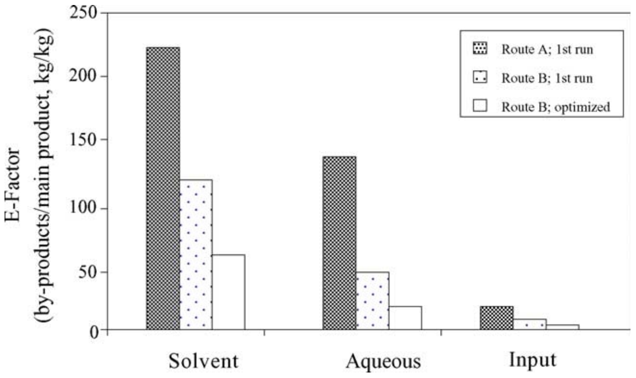

Fig. 1. Reduction of *E*-factor (by-products/main product ratio) by the optimization of synthetic route from A to B’s.